

CHAPTER 5

DISCUSSION

5.1 Appropriate basis set for the Li-C₆₀ complexes

In Table 4.1, the stabilization energies and the corresponding distances obtained from the STO-3G and 6-31G basis sets are significantly different. As one believes that the bigger basis set should lead to a more reliable results. However, it is clear that the DZP basis set is too big for the C₆₀ system. Use of the Boys-Bernardi counterpoise correction does not improve quality of both basis sets. Taking into account all the data in Table. 4.1, the 6-31G basis set is found to be suitable one for this system.

5.2 Intermolecular potential function

5.2.1 Li@C₆₀ endohedral potential function

As the endohedral interaction energies as a function of the C₆₀-Li separation are slightly positive at short distance and exponential growth when Li approaches close to the surface of the cage. This behavior can not be modeled properly by a simple analytical expression. From Fig. 4.2, the ΔE_{FIT} doesn't represent the SCF data. The fit for endohedral complex needs to be improved.

5.2.2 LiC₆₀ exohedral potential function

Exohedral stabilization energies behaves as usual, displaying strong positive at short distance and decaying to zero after about 5 Å for all trajectories (Fig. 4.3). Good agreement between the ΔE_{FIT} and ΔE_{SCF} is shown in Fig. 4.4(a) for all exohedral data and in Fig. 4.3(b) for optimal trajectory C6.

5.3 The Approximation of collision energy between Li and C₆₀ to form Li@C₆₀ complex

Figure 4.5, stabilization energy, extrapolated from the fit for each trajectory, shows an exponential growth when Li moves from the center to the surface of the cage and exponentially decay after going through the surface. The endohedral (before the maximum) and exohedral (after the maximum) are unsymmetric. Maximum of the peak, where Li lies on the surface and hence the highest repulsion between the two particles ($V(x_0)$) takes place, are 177.06, 28.86, 55.00 and 174.86 eV for the B66, C6, C5 and B65 trajectories, respectively.

Considering threshold energy data, it is clear that the easiest pathway for Li to enter the cage of C₆₀ is to penetrate through the hexagon, trajectory C6 (Fig. 4.6 and Table 4.4). The corresponding threshold energy is 28.23 eV. These values for C5, B65 and B66 are 54.01, 172.41 and 174.58 eV, respectively. As expected, very high collision energy is required in order to enter the cage through the C=C (B66) and C-C (B65) bonds. The finding is in good agreement with that found by Weiss [32] in which collision of Li and C₆₀ causes the lost of C₂ fragments from the C₆₀. By means of molecular dynamics simulation [58] and experiment investigation [59], lithium ion was found to enter the C₆₀ cage via the six membered ring. The collision energy for both observations are 5.9

and 6.0 eV, respectively. These values are about 5 times less than that of 28.23 eV for lithium atom observed in our study. As a consequence of the presence of higher number of electron on Li than Li^+ , higher energy would be required to penetrate through the surface of the C_{60} . Similar investigation has been done for the Li^+C_{60} complex in order to seek for reliability of the LiC_{60} system. The obtained stabilization energy at 3.9 Å on the trajectory C6 (tested calculation was carried out only for one configuration) of 1.58 eV is much lower than that of 6.84 eV for the LiC_{60} complex. This indicates considerable difficulty for Li to penetrate through the C_{60} surface compared to Li^+ .

5.4 Electron distribution in the Li-C_{60} complexes

Endohedral complex:

Fig. 4.7, change of atomic net charge on Li has been clearly displayed. When Li moves close to the surface, from center of the cage, atomic net charge on Li decrease smoothly. This is caused primarily by an increase of electronic repulsion due to valence electron of Li and of C_{60} .

Change of atomic net charges on carbon atoms for each trajectory are displayed in Fig. 4.9 - 4.12. Significant change takes place for specific sets of carbons, which lie around the vectors parallel to the trajectories (Table 4.5), e.g. carbon number 13, 21, 29, 37, 45 and 53 for trajectory C6 (see Fig. 3.3 for atomic labels).

As a function of C_{60} -Li distance, electron density of the carbon atoms around the trajectories increases (Fig. 4.9 - 4.12). The reason for this fact is that when Li is near the center of the cage, the repulsive forces between Li and C_{60} are small. Therefore, electron transfer can take place easily. However, the transferred electron has to be shared by almost all carbon atom of the C_{60} . This leads consequently to small increase of electron density on almost all carbon

atom. When Li is near the surface of C_{60} , repulsive forces increase thus, Li donates less electron to the C_{60} (Fig. 4.8). However, this electron distributes only in the specific area around the trajectories (Table 4.5). This makes significant change of the net charge of the carbon atoms of C_{60} at this region. As can be seen from Table 4.5, only 5 and 6 carbon atoms of the five and the six membered rings exhibit significant change of the net charges when Li approaches the surface at the center of the pentagon and the hexagon, respectively. For the B65 trajectory, such change takes place at bridging site of the six and the five membered ring, similarly for B66. In conclusion, Li approaching the surface at C6 and C5 sites donates its valence electron to carbon atoms of the central rings while Li at B66 and B65 sites transfers electron to the rings and the adjacent bridging sites.

Exohedral complex:

Change of electron density on Li for exohedral complex is different from that of endohedral one. Donation of $2s$ electron from Li is nearly impossible when Li is very close to the surface (Fig. 4.8). The reason is clearly due to the repulsion between electrons of the 2 monomers. Optimal donation takes place at medium distance and decays to zero at long distance. Characteristics of the electron transfer is somehow similar to the endohedral case. Valence electron of Li doesn't transfer homogeneously to the outer surface of the C_{60} but locates on some specific areas, depending on the moving path of Li. In the C5 and C6 trajectories where Li approaches to center of the five and the six membered rings, respectively, situation is exactly the same as that of the endohedral complex. For the trajectory through the bonds, B65 and B66, distribution of the $2s$ electron of Li localizes only on the two carbon atoms of the C-C and the C=C bonds, respectively. It is interesting to note that $2s$ electron of Li in exohedral complex spreads covering less number of carbon atoms than the

endohedral one. The reason is that distances from Li to these carbon atoms in endohedral complex are about the same because Li lies in the inner side of the curvature. For the exohedral case, Li stays on the outer side of the curvature. Only 2 carbon atoms, which lie on the two ends of the vector perpendicular to the B65 and B66 trajectories, are close to the Li. Therefore, transferred electron is almost localized only on the two nearest carbon atoms.

As Li influences only small part of the C₆₀ therefore, it is interesting to note that one can use only a small part of C₆₀ is sufficient to be the tested model, especially for *ab initio* calculations. This will assist in reducing computational cost which also allows the use of bigger and reliable basis set.

5.5 Effect of dipole moment on stability of the Li-C₆₀ complexes

Follow the Gauss' law, electrostatic potential inside a uniform spherical shell of charge is $\frac{q}{4\pi\epsilon_0 a}$ when q and a are atomic net charge and radius of spherical shell, respectively. The movement of Li inside or outside the C₆₀ cage and the change of the net charges of C₆₀ are the analog of this theorem.

Endohedral complex:

Dipole moments of the Li@C₆₀ endohedral complex for different trajectories are shown in Fig. 4.17, displaying important role on stability of the complex. Dipole moment surface-plot for all distance shows a maximum on the trajectory C6. This indicates a prevailing of the electron transfer in C6 than the other pathways. As a function of distance dipole moment of the complex increases when Li lies close to the surface. These characters are, again, shown for each trajectory in Fig. 4.18. Change of the endohedral stabilization energy is also given for comparison. When Li moves from the center to the surface of C₆₀

cage the charge of the surface increases, and also the potential energy and dipole moment of the complex as well (Fig. 2.18). This plots agree the Gauss' law very well.

It is seen from Fig. 4.18 that repulsion energies at the bridging sites, B65 and B66, are higher than those of the open sites, C5 and C6. For the dipole moment, an order is altered. This is caused by a higher polarizability of the complex where Li is on the open sites than the bridging sites. Compare C5 and C6, the stabilization energy along C6 is lower than that of C5 while their dipole moments don't differ significantly. When lithium atom was encapsulated in the cage of C_{60} , lithium releases $2s$ electron to C_{60} , this leading to the formation of lithium cation. Considering the optimal pathway, C6, the minimum of the energy curve takes place when an attractive forces, due to the polarization of the cage, are counterbalanced by the nuclear repulsion between the ion and the cage wall. The corresponding distance can be estimated from the ionic radii of the Li and van der Waals "radius" of the cage wall (precisely of carbon atom), which are 0.68 \AA and $1.47 - 1.76 \text{ \AA}$, respectively [60]. Thus, estimated distance to the energy minimum of the C6 pathway is to subtract radius of the cage by those two values, resulting 1.3 \AA from the center of cage. This is in good agreement with that shown in Fig. 4.18.

Exohedral complex:

Fig. 4.8, interaction energy decreases as a function of C_{60} -Li distance. In consistent with the change of atomic charges on carbon atoms of the C_{60} , dipole moment of the exohedral LiC_{60} complexes for all trajectories increases exponentially at short distance, displays a maximum at medium distance, then decays slowly to zero afterward. Changes of dipole moment is separately plotted in Fig. 4.20. No significant difference is found among the 4 trajectories as far as position of the maximum and absolute value of the dipole moment are

concerned. In term of stabilization energy (Fig. 4.20), they decay exponentially as a function of distance. However, trajectory C6 is still the optimal pathway for Li to approach the C₆₀.

Taking into account the energy data for both endohedral and exohedral complexes, C6 is the optimal pathway for both cases. In addition, exohedral interaction energy is less positive than the endohedral one. The reason is that Li in endohedral complex is restricted in specific area in the cage.

5.6 Optimized structures and properties of exohedral complexes

In order to investigate more details on the geometrical and electronic structure and related properties of the complexes, *ab initio* self-consistent field calculations were performed to optimize the C-C and C=C bond lengths and, the C₆₀-Li distances in the Li_nC₆₀; n = 1 - 6 and 12 complexes, using STO-3G and 6-31G basis set within UHF method. The geometries were entirely optimized within the selected symmetry point groups due to the following criterions;

- if possible lithium atoms must locate at C6 sites of which is the first priority, if not C5 sites as the next lower priority,
- lithium atoms must not be on the bridging sites, and
- the complex symmetry should be explicitly exploited as much as possible.

Each calculation requires 1-2 weeks (CPU time) on the DEC-Alpha Workstation, thus depending on the symmetry and number of Li atom. Results of the optimizations are collected in Table 4.8 and plotted in Fig. 4.21.

As shown in Table 4.8, the optimized bond lengths of the C₆₀ obtained from the STO-3G basis set are C=C = 1.375 Å and C-C = 1.448 Å. The corresponding values for the 6-31G basis set are 1.370 Å and 1.458 Å, respectively. They are in good agreement with the x-ray diffraction data [1]

(C=C = 1.355 Å and C-C = 1.467 Å). Furthermore, the HOMO-LUMO energy gaps are 8.6518 eV for the STO-3G and 7.5562 eV for the 6-31G. The experiment value is 4.91 eV [12]. Discrepancy between calculated and experimental results is clearly due to the basis set used. As can be seen from Table. 4.8, the bigger basis set, 6-31G, yields better HOMO-LUMO energy gap. It is expected from these results that experimental value could has been reached if the bigger basis set could has been applied. Unfortunately, the size of the system under consideration does obviously not allow the use of more extended basis sets because of tremendous increase in computation time. As can be seen from Table 4.1, the DZP basis set requires more than 150 hours, CPU time, for one point calculation.

Effect of the Li on the structural and electronic properties of the Li_nC_{60} complexes were summarized as follows.

i) LiC_{60}

The geometrical optimization was performed and the symmetry was restricted to C_{3v} , i.e., Li was moved along the vector perpendicular to center of the hexagon (Fig. 4.21(a)). Valence orbital, t_{1u} , of the C_{60} is splitted into $a_2 + e$ orbitals. The optimal C_{60} -Li distance is 7.38 Å with the shortest Li-C distance of 4.40 Å for 6-31G basis set. The corresponding values obtained from the STO-3G basis set are 5.24 and 2.33 Å, respectively. Swell of the cage in the LiC_{60} complex was detected. With respect to C_{60} , the double bonds extend from 1.370 to 1.376 Å (STO-3G) or 1.375 Å (6-31G) and the single bonds from 1.448 to 1.463 Å (STO-3G) or 1.452 Å (6-31G).

ii) Li_2C_{60}

Two lithium atoms were positioned on the vectors perpendicular to the center of the hexagons, leading to the D_{3d} symmetry of the complex (Fig. 4.21

(b)). The two distances between the lithium atoms and the center of the cage were optimized simultaneously. The obtained values are 5.47 Å (STO-3G) and 7.28 Å (6-31G). The ground state of the Li_2C_{60} complex is a triplet one in which the two valence electrons of the two lithium atoms occupy the e_u orbital (it is splitted from the t_{1u} LUMO of the C_{60}). Structure of the C_{60} was distorted by the two electrons, the single and the double bonds are 0.004 and 0.002 Å longer than that of C_{60} for the STO-3G basis set and 0.004 and 0.006 Å for the 6-31G basis set, respectively.

iii) Li_3C_{60}

Three lithium atoms are put around the cage of the C_{60} in the way to generate as high symmetry as possible, each lithium atom is on the normal vector of the pentagon. The principle axis (C_3) is on the normal vectors of the opposite hexagons (C_{3v} symmetry in Fig. 4.21(c)). The obtained C_{60} -Li distance for the three lithium atoms is 5.51 Å by the STO-3G and 7.59 Å by the 6-31G. The ground state is a quartet $a_2^1e^2$. The three lithium atoms transfer all three electrons to the C_{60} . Influence of the three electrons leads to an increase of the length of double and single bonds (compared to the C_{60}) to 1.376 Å (STO-3G) or 1.375 Å (6-31G) and 1.462 Å (STO-3G) or 1.452 Å (6-31G), respectively.

iv) Li_4C_{60}

One lithium atom was put on the top of center of the hexagon on the threefold axis of Li_3C_{60} , stated in (iii) (Fig. 4.21(d)). The resulted displacement of the Li from center of the cage is 5.60 Å for the STO-3G and 7.62 Å for the 6-31G. The t_{1u} orbital of the C_{60} splits to be a_2+e . The occupation pattern of valence orbitals is $a_2^2e^2$, that is triplet ground state. The cage of the C_{60} was deformed by the four $2s$ electrons. The length of the double and the single

bonds are 1.379 and 1.461 Å (STO-3G) or 1.374 and 1.452 Å (6-31G), respectively.

v) Li_5C_{60}

Another lithium atom was added to the normal vector of the opposite hexagon in the Li_4C_{60} complex (Fig. 4.21(e)). The optimal distance from Li to the center of the cage is 5.73 Å for the STO-3G and 7.88 Å for the 6-31G. The five $2s$ electrons from lithium atoms fill up the a_2+e orbitals. Slightly distort of the C_{60} structure due to the lithium atoms was also observed (Table 4.8).

vi) Li_6C_{60}

All lithium atoms locate on the top of the hexagons (Fig. 4.21(f)). The major axis is C_3 , lying through the opposite hexagons. The resulted symmetry of the complex is C_{3v} . The C_{60} -Li distance is longer (Table 4.8), than that of complexes of the smaller number of lithium atoms. The six electrons from the six lithium atoms occupy the a_2+e orbitals in configuration $a_2^1 a_2^1 e^2 e^2$. Change of C-C and C=C bond lengths are also found.

vii) $\text{Li}_{12}\text{C}_{60}$

The twelve lithium atoms are on the head of the twelve pentagons. (Fig. 4.21(g)). Symmetry of molecule retains the I_h symmetry. All electrons from lithium atoms are filled up in the $t_{1u}+t_{1g}$ orbitals. The electronic configuration is $t_{1u}^6 t_{1g}^6$. Deformation of the cage structure is taken place.

Taking into account all the data given above, the following conclusions have been made.

i) Although a slight changing of the C-C and C=C bond lengths was detected in the Li_nC_{60} complexes, relative to that of free ligands. However, it is

possible to conclude in all case that structure of the C_{60} is swollen due to the Jahn-Teller distortion.

ii) The complexes of more number of Li exhibit higher binding energy per lithium atom and longer C_{60} -Li distance. The STO-3G basis set yields a too short intermolecular distances in the Li_nC_{60} complexes. The appropriate distance of about half of the length of unit cell (7.06 Å) is proposed experimentally [20].

iii) The use of the STO-3G basis set yields higher HOMO-LUMO energy gaps for all Li_nC_{60} complex than those of the 6-31G. However, they are in a very good agreement, as the plots are about parallel that show minimum at the same position (Fig. 4.23). More detailed discussion has already been done in section 5.5.

5.7 Electronic structures of exohedral complexes

From MO diagram in Fig. 4.22 and the HOMO-LUMO energy gap plotted in Fig. 4.23, optimized structure of the C_{60} displays the energy gap of 8.6518 and 7.5562 eV obtained from the STO-3G and the 6-31G basis sets, respectively. When one lithium atom was added, 2s electron of lithium atom transfers to t_{1u} of the C_{60} resulting the spilt of t_{1u} to form a_2 and e orbitals with the reduction of symmetry from I_h to C_{3v} . Consequently, the energy gap decreases to 6.2417 and 4.8512 eV for the STO-3G and the 6-31G basis set, respectively. For the Li_2C_{60} complex, two electrons from the two lithium atoms occupy a e_u orbital and spin state of the complex is triplet. The energy gap for the STO-3G, is 5.8412 eV and for the 6-31G, is 4.3246 eV. In the case of Li_3C_{60} , the symmetry of molecule retains C_{3v} and the configuration of valence electron is $a_2^1e^2$ in quartet state. Furthermore, this complex causes the lowest energy gap of 5.3341 eV (STO-3G) or 4.1616 eV (6-31G). When Li was added

more, the Li_4C_{60} complex (C_{3v} symmetry) displays electron configuration of $a_2^2e^2$ in triplet state. Its energy gap of 6.0778 eV by the STO-3G and 4.6518 eV by the 6-31G are higher than those of the Li_3C_{60} (Fig. 4.23). Increase number of Li to form Li_5C_{60} , the complex retains C_{3v} symmetry and the energy gap is also increase. In the Li_6C_{60} complex, the 6 electrons of lithium atoms make the t_{1u} and t_{1g} orbitals of C_{60} splitting to $2(a+e)$ and fill up these orbitals. This complex shows the highest energy gap comparing to those complexes of $n = 1-5$. The last composition which is considered in this study is the $\text{Li}_{12}\text{C}_{60}$. Its symmetry remains that of the original symmetry of the C_{60} , i.e., I_h . All electron from lithium atoms full fill the t_{1u} and t_{1g} orbitals leading to the decrease of the energy gap (Fig. 4.22).

It is interesting to note that, conductivity of the Li_nC_{60} complexes which is inversely proportional to the E_g depends on the number of lithium atoms. In this study, the Li_3C_{60} shows lowest energy gap. With this composition, the three lithium atoms are well fitted to one octahedral site and two tetrahedral sites in the C_{60} crystal lattice. In addition, encapsulation of 3 lithium atoms leads to delocalization of the three electrons. They are also able to circulate over the whole lattice. The obtained result is in good agreement with that reported experimentally [5] for the conductivity of K_nC_{60} complexes that is the energy gaps are 1.0 and 1.6 eV for $n=3$ and $n=6$, respectively. For the Li_nC_{60} complexes where $3 < n \leq 6$, their conductivity decrease because of the excess number of lithium atoms. This leads to an increase of the C_{60} -Li distance or the length of the unit cell and decreases degree of delocalization of the electrons in lattice. For the $\text{Li}_{12}\text{C}_{60}$ complex, its conductivity as well as the C_{60} -Li distance are very similar to those of Li_4C_{60} , i.e., cluster size is smaller and conductivity is higher compared to Li_5C_{60} and Li_6C_{60} . This finding is supported by the molecular dynamics study [61] which signal the possibility that a cluster of the type $\text{Li}_{12}\text{C}_{60}$ may be stable.

Although the calculations predict well, as it is in good agreement with the experiment data [6], [38], the Li_nC_{60} composition where the lowest energy gap takes place ($n=3$). However, the predicted energy gaps obtained from these calculations are relatively high (Fig. 4.23). Use of bigger basis set would lead to slight decrease of the energy gap. As experimental data for this system is not available, it is inevitable to conclude from this data that the investigated Li_nC_{60} system is insulator as its conduction band is more than 1 eV higher than the valence band.



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